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Characterisation of isothiocyanic acid, HNCS, in the solid state: trapped by hydrogen bonding

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The crystal structure of [Ph₄P][NCS].HNCS is reported. This is the first structural determination of isothiocyanic acid and hydrogen bonding between the NCS anion and HNCS fragment explored using computational chemistry.

Isothiocyanic acid, HNCS, is a well-established interstellar molecule that was first detected by microwave spectroscopy in the gas cloud Sagittarius B2 (*Sgr B2*), close to the centre of the Milky Way.¹ Whilst the chemistry of the analogous HNCO has been well developed, HNCS has not been explored to a great extent. Early theoretical studies² on HNCS showed that of the 4 possible isomers HNCS, HSCN, HSNC and HCNS the most stable was HNCS. The next two isomers, thiocyanic (HSCN) and isothiofulminic (HSNC) acids were spectroscopically identified in low temperature matrix isolation experiments.³ Measurement of the rotational spectrum⁴ of HSCN, allowed this to be identified in both *Sgr B2*⁵ and the *Taurus Molecular Cloud 1*.⁶ The least stable isomer thiofulminic acid (HCNS) was only recently observed *via* photolysis in low temperature matrix.⁷ A number of spectroscopic studies on isothiocyanic acid have been reported including IR spectroscopy in the gas phase,⁸ organic solvents and water,⁹ and in a low temperature matrix;^{3,10} the shift of the N=C bond stretch compared to the anion [NCS]⁻ is found to be negligible. The structure of HNCS has been primarily elucidated through the analysis of microwave spectroscopy, initially with the assumption that this was linear¹¹ followed by more accurate spectra which showed a bending of the HNC fragment.¹² UV and ro-vibrational spectra of HNCS and DNCS have also been reported.¹³ Theoretical chemists have been active in this area with a number of studies reported of increasingly high level, culminating in CASSCF/CASPT2 calculations.¹⁴

Another interesting facet of the chemistry of HNCS is hydrogen bonding, which has been observed in matrix isolation studies in low temperature argon matrices of CO,¹⁵ N₂ and Xe,¹⁶ and as hydrogen bonded dimers in an N₂ matrix.¹⁷ However, given that HNCS is a gas that decomposes at room temperature,¹⁸ there has been no crystallographic evidence presented for any of the isomers.

As part of our recent investigations of uranium thiocyanate chemistry,¹⁹ we isolated a few pale red crystals that were shown to be [Ph₄P][NCS].HNCS, **1**, from the reaction of UCl₄ with Na[NCS] and Ph₄PCl. Notably the hydrogen position was located on the difference map as the highest remaining density peak and was allowed to refine without any constraints. Presumably HNCS is formed by surreptitious water or acid, and we were not able to determine the fate of the uranium. A rational synthesis was developed whereby [Ph₄P][NCS], **2**, was synthesised by the reaction of [Ph₄P][Cl] and Na[NCS] in MeCN. The addition of gaseous HNCS in the same solvent affords a colour change from

colourless to red over the period of 5 minutes and **1** can be isolated in high yields. Alternatively, passing gaseous HNCS over single crystals of **2** also gives **1**, albeit much more slowly and with loss of crystallinity; the identity was confirmed by IR and uv-vis spectroscopy and powder XRD.

1 represents the first determination of the crystal structure of HNCS; a coordination complex to a copper macrocycle was reported, but the hydrogen was not located and the assignment corroborated only on the basis of IR spectroscopy.²⁰ The molecular structure of **1** is shown in Fig. 1 and bond lengths in the HNCS fragment recorded in Table 1, along with those from theory and microwave spectroscopy. For comparison we also structurally characterised **2**, and the structure is shown in Fig. S1. The bond lengths in the anionic component in **1** [N(29)-C(28) = 1.147(3) Å; C(28)-S(2) = 1.623(2) Å], is typical for anionic, uncoordinated [NCS]⁻ ions,²¹ and in **2** the corresponding bond lengths are 1.128(4) Å for the N=C and 1.675(3) Å for the C=S bond. In the HNCS fragment the N=C bond lengthens slightly whilst the C=S bond is significantly shorter in the acid. The structure of **1** also shows a

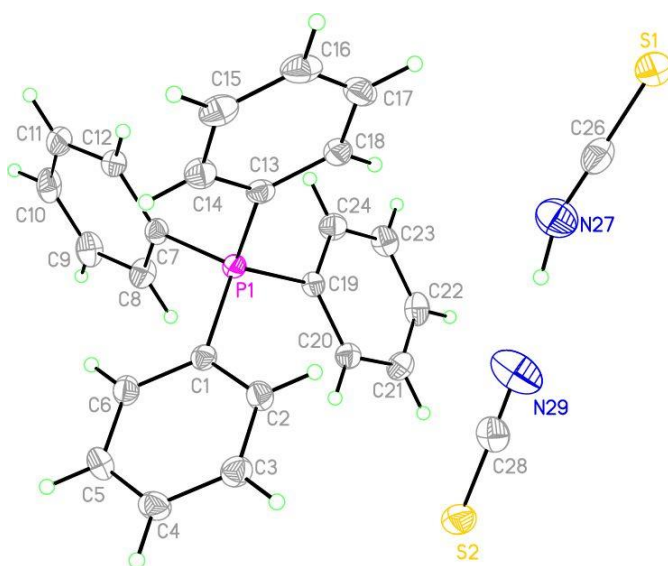


Fig. 1. Molecular structure of **1** with thermal displacement shown at 50% probability.

very short hydrogen bond of 1.60(3) Å, shorter than those calculated for the (HNCS)₂ dimer (H...N = 2.034 Å).¹⁷ From the solid state structures it is apparent that the N=C bond length is only slightly lengthened in isothiocyanic acid fragment, but surprisingly the C=S bond is shorter.

Given the uncertainty in refining a structure with a hydrogen atom next to a heavy atom, we sought to confirm this *via* spectroscopic methods. The infrared and Raman spectra of **1**

are shown in Fig. 2, along with that of NaNCS and **2** for comparison. In the IR spectrum the N=C peak is broad and distinctly asymmetric with a maximum at 2054 cm^{-1} and a shoulder at 2018 cm^{-1} ; the C=S stretch at 750 cm^{-1} is almost identical relative to **2** and Na[NCS]. Interestingly, a peak assignable to the N-H stretch is not observable, possibly due to the very strong hydrogen bond; this is further studied by DFT methods (*vide infra*). **1-d** was synthesised by the reaction of DNCS, synthesised from DCl and NaNCS, and **2** and the IR spectrum shows that the N=C peak narrows compared to **1** (Fig. S4-S5), suggesting that this band is due to both the N=C and N-H stretch. The Raman spectrum of **1** is more clear with two broad peaks observed in N=C region and the C=S stretch is slightly blue-shifted compared to **2** and Na[NCS], corroborating the structural data. ^1H NMR spectroscopy displays a broad resonance at 8.82 ppm in addition to the aromatic protons (Fig. S13). This is a large shift in comparison to $\text{HNCS}_{(\text{g})}$ dissolved in CDCl_3 at 5.49 ppm (Fig. S19), which is a triplet presumably due to coupling to ^{14}N .²² In the corresponding DNCS, there is a resonance at 0.94 ppm in the ^2H NMR spectrum (Fig. S20) and no resonances in the ^1H NMR spectrum, confirming our assignment. **1-d** was also examined by ^1H and ^2H NMR spectroscopy and confirms the large chemical shift to $\delta_{\text{D}} = 7.28$ ppm upon hydrogen bonding (Fig. S20). The isothiocyanate carbons are not seen in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, which is a common observation.²³ The UV-vis spectrum of **1** and **2** (Fig. S9 and S10) shows sharp features at 277 nm and 266 nm whilst **1** additionally displays a broad absorbance at 351 nm ($\epsilon = 24 \text{ M}^{-1} \text{ cm}^{-1}$) and 302 nm ($\epsilon = 24 \text{ M}^{-1} \text{ cm}^{-1}$). Finally TGA-IR measurements were conducted on **1** and HNCS detected after heating to 95 °C (Figs. S11-S12), indicating that although the hydrogen bonded complex is stable, it decomposes at relatively low temperatures. However at room temperature **1** retains its stability as a crystalline solid at room temperature for at least 6 months.

Given the interesting structural parameters, we have explored the structure and bonding of **1** using dispersion-corrected DFT (Table 1). The optimised geometry reflects the

Table 1. Comparison of bond lengths (Å) and angles (°) for HNCS from experiment and theory.

	1	1 DFT	CASSCF of HNCS ¹⁴	Microwave of HNCS ^{12c}
N-H	0.98(3)	1.099	1.009	0.993(6)
N-C	1.162(2)	1.173	1.206	1.207(3)
C-S	1.6033(19)	1.618	1.591	1.567(1)
H-N-C	160(2)	164.8	134	131.7(19)
N-C-S	178.93(19)	179.0	173.6	173.8(23)
H...N	1.60(3)	1.488	-	-
N...N	2.577(2)	2.585	-	-

experimentally determined metric parameters well, confirming the stability of the trimolecular complex and the assignment of hydrogen positions. A strong N—H...N hydrogen bond is indicated by H...N and N...N distances, the latter in excellent agreement with crystallographic data. DFT data also supports the bending of the H-N-C linkage in **1**. It appears that this non-linear structure of HNCS is influenced strongly by the crystalline

environment, since the tetraatomic HNCS optimised at the same level of theory exhibits an angle of 134.4° (in agreement with experiment and high-level *ab initio* prediction)

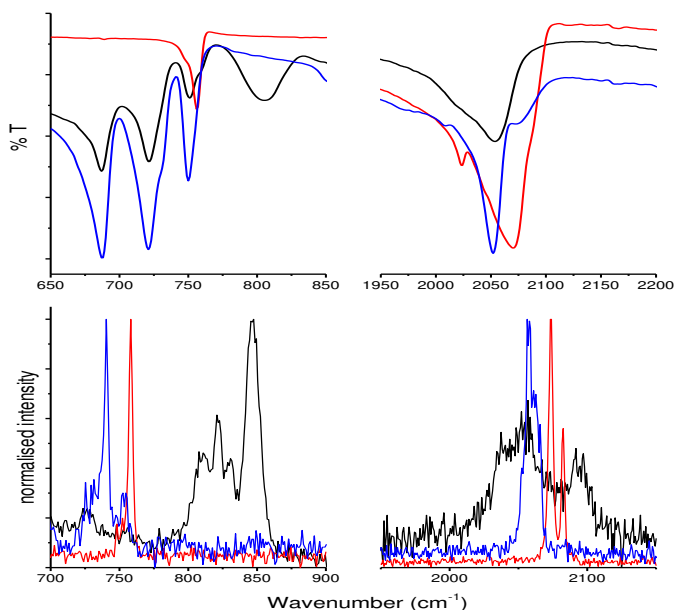


Fig. 2. Infrared (top) and Raman (bottom) spectrum of **1** (black), NaNCS (red) and **2** (blue) in the solid state.

whereas the hydrogen bonded dimer $[\text{SCN}\cdots\text{HNCS}]^-$ complex is linear (H-N-C = 179.6°).

Predicted IR and Raman spectra (Fig. S6 and S8) give qualitative insight into the experimental data in Fig. 2.²⁴ Normal modes of **1** with greatest N-H motion occur at 2380 and 1899 cm^{-1} , the former strongly coupled with N-C stretching mode and the latter more like “pure” N-H stretch. These values are massively red-shifted from the predicted value for free HNCS (3776 cm^{-1}), but slightly blue-shifted from the calculated $[\text{SCN}\cdots\text{HNCS}]^-$ dimer (2311 and 1380 cm^{-1}). C-S stretching in **1** is predicted to occur at 775 cm^{-1} , compared to 886 and 716 cm^{-1} in HNCS and $[\text{SCN}\cdots\text{HNCS}]^-$, respectively. Structural and spectroscopic data therefore suggest a strong N-H...N hydrogen bond in **1**, but one that is not as strong as in the hypothetical $[\text{SCN}\cdots\text{HNCS}]^-$; perhaps due to the constraints of the crystalline environment. To examine hydrogen bond strength in more detail, we carried out binding energy and atoms in molecules (AIM) analysis on **1**. The counterpoise corrected binding energy of the $[\text{SCN}\cdots\text{HNCS}]^-$ dimer extracted from **1** is predicted to be -104.9 kJ mol^{-1} , *i.e.* within the range of “very strong hydrogen bonding” and consistent with the large red-shift noted above. The value of the electron density at the critical point, ρ_{bcp} , often taken as a proxy for bond strength, is also very large in the H...N bond in **1** at 0.082 e.bohr^{-3} ,²⁵ while the weakening of the donor N—H bond is evident from the ρ_{bcp} of 0.243 e.bohr^{-3} , compared to a value of 0.334 e.bohr^{-3} in isolated HNCS.

In summary, we have been able to “trap” HNCS via strong hydrogen bonding to a thiocyanate anion and have structurally characterised this for the first time. DFT calculations shed further light on the bonding and AIM confirms the strong hydrogen bond.

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